

Report Title:

Enhanced Hydrogen Production Integrated with CO₂ Separation in a Single-Stage
Type of Report: **Annual Technical Progress Report**

Reporting Period Start Date: October 1, 2005

Reporting Period End Date: September 30, 2006

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Report Issue Date: October, 2006

DOE Contract No: **DE-FC26-03NT41853**

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ABSTRACT

Enhancement in the production of high purity hydrogen from fuel gas, obtained from coal gasification, is limited by thermodynamics of the Water Gas Shift Reaction. However, this constraint can be overcome by concurrent water-gas shift (WGS) and carbonation reactions to enhance H_2 production by incessantly driving the equilibrium-limited WGS reaction forward and in-situ removing the CO_2 product from the gas mixture. The spent sorbent is then regenerated by calcining it to produce a pure stream of CO_2 and CaO which can be reused. However while performing the cyclic carbonation and calcination it was observed that the CO_2 released during the in-situ calcination causes the deactivation of the iron oxide WGS catalyst. Detailed understanding of the iron oxide phase diagram helped in developing a catalyst pretreatment procedure using a H_2/H_2O system to convert the deactivated catalyst back to its active magnetite (Fe_3O_4) form. The water gas shift reaction was studied at different temperatures, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0-300 psig. The combined water gas shift and carbonation reaction was investigated at temperatures ranging from 600-700C, S/C ratio of 3:1 to 1:1 and at different pressures of 0-300 psig and the calcium looping process was found to produce high purity hydrogen with insitu CO_2 capture.

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EXECUTIVE SUMMARY

Enhancement in the production of high purity hydrogen from fuel gas, obtained from coal gasification, is limited by thermodynamics of the Water Gas Shift Reaction (WGSR) which is used to shift the carbon monoxide towards hydrogen. However, this constraint can be overcome by concurrent water-gas shift (WGS) and carbonation reactions to enhance H_2 production by incessantly driving the equilibrium-limited WGS reaction forward and in-situ removing the CO_2 product from the gas mixture. The in-situ incessant removal of carbon dioxide is achieved by using a calcium oxide sorbent via the high temperature carbonation reaction that augments the WGSR towards H_2 production. The WGSR is achieved by the High Temperature Shift (HTS) iron oxide catalyst while the CO_2 capture, in this investigation, was achieved using the OSU patented precipitated calcium carbonate sorbent which has demonstrated superior performance over other naturally occurring calcium sorbents. To date, we have investigated the performance of the sorbent towards high temperature CO_2 capture, high purity hydrogen production via the sorbent catalyst mixture at high temperatures and the regeneration of the spent sorbent under sub-atmospheric condition to generate a pure sequestration-ready CO_2 stream.

However it was observed that the performance of the HTS catalyst and calcium oxide system, towards H_2 production deteriorates over multiple cycles due to the deactivation of the HTS catalyst (iron oxide) by the CO_2 gas that is evolved during the high temperature calcination phase. A thorough investigation of the HTS (iron oxide) catalyst composition was conducted and a pretreatment procedure was developed which reduces the oxidized form of the catalyst to the required active phase. The active phase of the HTS catalyst is Magnetite (Fe_3O_4). However, in the presence of an oxidizing atmosphere, like pure CO_2 , the magnetite phase gets oxidized to the hematite (Fe_2O_3) form which is likely during the calcinations step. This is evident from the iron oxide phase diagram for CO- CO_2 system. Thus, the pretreatment step consists of treating the oxidized catalyst to a reducing H_2/H_2O mixture at 600 °C which reduces the Hematite (Fe_2O_3) form back to the active Magnetite (Fe_3O_4) form. This fact was confirmed by X-ray diffraction analyses of the HTS catalyst before and after the pretreatment procedure. Multicyclic runs which consist of combined WGS/carbonation reaction followed by in-situ calcination with a subsequent catalyst pretreatment procedure sustains the catalytic activity and prevents deactivation.

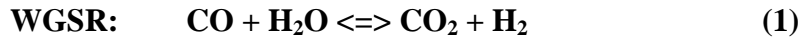
The baseline WGSR was investigated at different temperatures (450–750°C), different steam to carbon monoxide (S/C) ratios (3-1) and different total pressures (0-300 psig) to determine the optimum conditions for maximum WGSR catalytic activity under these varying conditions. The HTS iron oxide catalyst, procured from Sud Chemie, was used for these tests. The CO conversion showed a maximal where it rises with increasing temperature up to a critical temperature beyond which it dropped monotonically. It was also observed that the CO conversion increased with S/C ratio and total pressure. In addition, it was observed that the system approached equilibrium more closely with an increase in the temperature and total pressure while the system moved away from equilibrium with an increase in the S/C ratio.

The combined water gas shift and carbonation reaction was investigated at high pressures using the proprietary calcium based sorbent (PCC) under the optimal conditions of operations

determined earlier by the catalytic experiments. The combined reactions were studied at temperatures ranging from 600-700 °C and S/C ratios of 3:1, 2:1 and 1:1, and at various pressures ranging from 0 to 300 psig. It was found that the CO conversion for the combined reactions increases with an increase in the total pressure resulting in an increase in the purity of the hydrogen produced. It was also found that with an increase in the S/C ratio the CO conversion increases at atmospheric pressures but at high pressures the increase in the S/C ratio does not have any significant effect on CO conversion. Thus high pressure operation favors the reduction of excess steam in the system while maintaining its CO conversion. In another investigation, it was observed that the CO conversion at high pressure operation (300 psig) is not affected by varying reaction temperature for an S/C ratio of 3:1 but for lower S/C ratios of 1:1, a temperature of 600 °C was found to be most favorable. Hence the calcium enhanced WGSR process provides a one box approach for the production of high purity hydrogen with the simultaneous removal of CO₂.

INTRODUCTION

The rising energy demand coupled with the depleting global oil reserves and the environmental degradation due to emissions has led to extensive research in the field of clean energy production. Coal is present in abundance in the United States totally around 270 billion short tons. Although coal gives rise to harmful emissions it can be used to provide a major portion of our energy needs if the syngas produced can be cleaned in an energy efficient manner. Hydrogen is produced from coal through gasification which more efficient and leads to a lesser amount of emission than combustion (Fan et al, 2006). The syngas produced from gasification is then sent to the water gas shift reactor to enhance the hydrogen content of the stream by shifting the CO to CO₂. The water gas shift reaction (WGSR) plays a major role in increasing the hydrogen production from fossil fuels. The hydrogen production is limited by thermodynamic constraint posed by the equilibrium limitation of the WGSR. However, this constraint can be overcome by concurrent water-gas shift (WGS) and carbonation reactions to enhance H₂ production by incessantly driving the equilibrium-limited WGSR forward and by in-situ CO₂ removal from the product gas mixture. This process can effectively and economically produce a pure H₂ stream by coal gasification with integrated capture of CO₂ emissions, for its subsequent sequestration. The reaction schemes involved are as follows:



While various calcium oxide precursors were tested for CO₂ capture, naturally occurring limestones were unable to react completely due to pore pluggage and pore-mouth closure (Gupta and Fan, 2002). However, the highly reactive mesoporous precipitated calcium carbonate (PCC) particles, synthesized by a novel wet precipitation technique using surface modifiers, can achieve up to 70 wt% capture during carbonation. Life cycle testing of the sorbent over multiple cycles of carbonation-calcination reactions showed that PCC sorbent attains a capture capacity of 40-36 wt% over 50-100 cycles, which is significantly higher than most of the other high temperature sorbents reported in literature (Iyer et al., 2004). In contrast, naturally occurring limestone (LC) shows poor performance.

The enhanced water gas shift reaction for H₂ production with *in-situ* carbonation was studied using High Temperature Iron Oxide Shift (HTS) catalyst and calcium sorbents. Experimental evidence clearly shows that the PCC sorbent demonstrates superior performance over that of naturally occurring limestone sorbents. Gas composition analyses show the formation of pure hydrogen stream during the initial part of the breakthrough curve, thus demonstrating the synthesis of pure hydrogen. To date, in this project, the reactions were investigated over reaction temperatures ranging from 500-750 °C at ambient pressures. The current focus is to conduct these experiments at high pressures varying from 1-20 atm. In addition the effects of varying the steam to carbon monoxide ratios is also investigated. The incessant removal of CO₂ from the water gas shift reaction not only enhances the hydrogen production process but it also reduces the requirement for excess steam to drive the WGS forward. Thus, operating at conditions involving near-stoichiometric steam requirements augments the H₂S removal by CaO.

WGS iron oxide catalyst: phase diagram and deactivation

It is evident from previous reports (Annual report, Sept 2004) that the performance of the HTS-CaO system deteriorates over multiple WGS-carbonation and calcination cycles. This is due to the deactivation of the HTS catalyst by the CO₂ gas that is evolved during the calcination phase. In our previous report (Semi-Annual Technical Progress report, March 2005) we had designed a novel multi-fixed bed reactor system which avoids the contact of CO₂ with the WGS catalyst system during the calcination phase. Hence in this quarter, a novel approach to understand the WGS catalyst phases and its deactivation was undertaken.

It has been suggested in literature that exposing the commercial iron oxide/chromium oxide catalyst to high operating temperatures leads to a decrease in the kinetics of the high temperature shift catalyst (Bohlbro, 1969; Newsome, 1980). The deactivation of the catalyst is a result from different phenomena occurring during the operation of the commercial catalyst under the water-gas shift conditions. Keiski and Salmi (1992) found that operating close to industrial temperature of 575-723 K led to a decrease in catalytic activity due to a sintering process. The deactivation of the catalyst was most active during the first 150 hours and the decay of the catalyst was linked to a decrease of the surface area and to an increase of the mean pore size of the catalyst.

The commercial catalyst of iron oxide/chromium oxide is a catalyst that can undergo bulk phase conditions when exposed to different atmospheres. The active phase of the catalyst is magnetite (Fe_3O_4). However, during the calcination step of the WGS-carbonation and calcination process, pure CO_2 is released from the calcium carbonate and the water gas shift catalyst is exposed to an oxidizing atmosphere of 100% CO_2 at 700°C . According to the thermodynamics of iron oxide under various gas compositions and temperatures, the iron oxide catalyst is oxidized from magnetite to hematite (Fe_2O_3), an oxidized form of iron oxide. Since the active bulk phase of the catalyst is magnetite, the iron oxide catalyst needs to be reduced from hematite to magnetite. According to the thermodynamic plot of iron oxide in a hydrogen-steam system, iron oxide becomes magnetite when exposed to a reducing atmosphere of 20% H_2 and 80% H_2O at 600°C .

Rethwisch et al. (1985) studied the water-gas shift reaction at 660 K on both unsupported magnetite and magnetite particles supported on graphitic materials. They found that exposing the catalyst to a 15% $\text{CO}/85\%$ CO_2 gas mixture at 660 K for 22 hours could restore high catalytic activity, but no significant increases were found in a 40% $\text{H}_2/60\%$ H_2O gas mixture for 22 hours. The CO/CO_2 treatment step resulted in a 200-300% increase in activity through a water-gas shift condition of 64% H_2O , 32% CO , and 4% CO_2 .

High Pressure Hydrogen Production

To obtain high purity H_2 , the WGS reaction is generally carried out in two stages (Gerhartz, 1993; Bohlbro, 1969): (1) high temperature shift ($250\text{--}500^\circ\text{C}$) using iron catalysts and (2) low temperature shift ($210\text{--}270^\circ\text{C}$) using copper-based catalysts. Copper based catalysts are extremely intolerant to small quantities of sulfur ($< 0.1\text{ppm}$) and hence the fuel gases need to be desulfurized upstream of the WGS reactor. A high steam: CO ratio is required to enhance CO conversion and the consequent hydrogen production. The steam to CO ratio at 550°C can be as high as 50 in a single-stage operation or 7.5 for a more expensive dual-stage process to obtain 99.5 % pure H_2 (Newsome, 1980). For example, to lower the CO content of the typical fuel gas from 45 % (inlet) to 3% (outlet) a total steam addition of 1.18 kg/m^3 of the gas is required, at a total pressure of 60 bars and 410°C (Gerhartz, 1993). While higher temperature enhances the kinetics of the WGSR, thermodynamics adversely affects the

hydrogen production due to the equilibrium limitation of the WGSR with the H_2 yield falling with rising temperature.

Enhancing the Water gas Shift Reaction and Hydrogen Purification

An effective technique to shift the WGSR to the right for enhanced hydrogen generation has been to remove hydrogen from the reaction mixture. This premise has led to the development of hydrogen separation membranes. However, membranes cannot completely remove hydrogen from the mixture and there is also the effect of a considerable pressure drop across them (Roark, et al 2002). In addition, any remaining hydrogen in the main stream would dilute CO_2 and would lead to poor process economics.

The other option is to remove the CO_2 from the reaction gas mixture. Various solvents such as amines, Selexol, Rectisol etc have been used to scrub the CO_2 from the WGS reaction gas mixture (Steigel and Ramezan, 2006) between two stages. However, these solvents operate at ambient temperatures and consequently this method involves severe energy penalties due to cooling and reheating of the reaction gas mixture. Hence, high temperature CO_2 membranes were developed (US DOE, 2005) which operate in the same temperature range as that of the WGSR. Thus the development of these membranes has led to the concept of membrane reactors. However, the use of these membranes leads to the development of a pressure drop and the costs associated with these membranes make the overall process expensive.

Calcium Assisted Hydrogen production

There are several processes that enhance hydrogen production using limestone sorbents such as the ZECA process and the HyPr-RING Process (Lin et al., 2002; Ziock et al., 2001). However, these processes operate at very high pressures (12-100 MPa) to produce H_2 , which is not economically viable. On the other hand processes such as HyPr-RING result in the gasification of coal with in-situ CO_2 capture using $CaO/Ca(OH)_2$ systems (Lin et al., 2005). However, these systems operate at very high pressures (70 bar) and require excess steam and produce only 91% pure hydrogen. In addition, there have been several reports on sorption enhanced hydrogen production by coupling SMR and in-situ CO_2 capture using a sorbent (Hufton et al., 1999; Akiti 2004; Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 2001). Calcium oxide assisted steam methane reforming (SMR) was attempted in earlier studies (Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 2001). They detailed

the performance of a single-step sorption-enhanced process using a Ni-based catalyst to produce hydrogen. However they also mixed dolomite-CaO powder with the Ni-based catalyst to separate CO₂ and enhance H₂ concentration to 97%.

Our proposed process under consideration involves removing CO₂ from the gas mixture by reacting it with CaO (carbonation), which can be conducted at high operating pressures. Albeit, higher pressures and temperatures lead to thermodynamic equilibrium, the constant removal of CO₂ drives the reaction forward, resulting in enhanced kinetics and improved H₂ yield.

Sulfur Removal

The main drawback, which all the hydrogen production processes do not address, is the effect of sulfur in the feed. Sulfur is present in syngas in the form of H₂S and COS. According to equilibrium calculations at temperatures below 1300K all sulfur radicals combine to form predominantly H₂S which is close to 95% of the total sulfur content and COS forms the other 5%. (M.Jazbec et al, 2004) This process aims at removing the sulfur (H₂S and COS) in the system using the high reactivity calcium oxide sorbent, which is also used to capture CO₂ in the WGS reactor to produce hydrogen.

Sulfur removal using Calcium based sorbents

Of the metal oxides that can be used as H₂S capture sorbents, calcium has the third smallest equilibrium limitation only after V₂O₃ and ZnO, and even these cannot be used at temperatures greater than 650°C (Hartman et al, 2002). In addition, limestone is also cheap and abundant in nature. Hence, extensive research has been conducted to use calcium-based sorbents for gas clean up applications.

Calcined limestone has been found to be a better sorbent for H₂S removal than uncalcined limestone as calcination of CaCO₃ increases the porosity by releasing CO₂ which escapes from the sorbent matrix leaving behind lower molecular weight CaO. (Yrjas et al, 1996) Calcined limestone reacts with hydrogen sulfide to form calcium sulfide as shown below in eqn (4), which has a greater molar volume than calcium oxide.



Hence the effect of pore structure, temperature and partial pressure of hydrogen sulfide has been studied on the sulfidation of calcined limestone. Sulfidation has been found to increase

with temperature and partial pressure of H_2S (Adenez et al, 1998, Hartman et al, 2002, Garcia-Labiano et al, 2004) and even after the complete conversion of the CaO to CaS the reacting particle (calcined limestone) remains significantly porous (20%). (Hartman et al, 2002) It has been unanimously agreed upon that the conversion achievable by the sorbent is mostly depended of the pore structure created after calcination.(Adenez et al, 1998) It is taken as a rule that a material sinters at a temperature 0.6 times its temperature of fusion.(Fenouil et al, 1994) It was found that natural limestone sintered when it was calcined at high temperatures making it unfit for sulfur removal and multicyclic use.(Ruth et al,1984, Borgwardt et al, 1984). Fenouil et al also confirmed that CaS formed did not sinter in the presence of N_2 or H_2 but it sintered in the presence of CO_2 (Fenouil et al, 1994) Hence if calcium oxide is used in the system both H_2S and CO_2 will be removed and hence there will be no build up of CO_2 in the system to cause sintering of the sorbent. Also in all these systems both calcination and sulfidation have been studied at very high temperatures hence sintering effects seem to be very prominent. If these two reactions can be conducted at lower temperatures with a sorbent that has a good pore structure sintering may be avoided.

EXPERIMENTAL

Modification of integral fixed bed reactor system for high-pressure operation

The existing reactor setup (described earlier in Annual report, Sept 2005) was modified to handle high pressures of up to 20 atmospheres. A back-pressure regulator procured from Swagelok (KPB series) was installed in the setup to build pressure within the reactor. This back pressure regulator is capable of building pressures of up to 68.9 atm (1000 psig). The valve seat material is made of PEEK which is corrosion resistant to acidic hydrogen sulfide vapors, which makes it capable of conducting H_2S experiments. As shown in Figure 1 below, the inlet of the backpressure regulator is connected to the reactor rod and the outlet is connected to a heat exchanger. Since the entire section of the equipment setup upstream of the backpressure regulator will be exposed to high pressures various components were replaced to make the setup capable of handling pressures of as high as 20 atms. Flow meters previously used to adjust the flow rates of the reactant gases were replaced by mass flow controllers procured from Brooks Instruments (model 5850E). Teflon pipes used for carrying the reactant gases to the reactor and the water from the pump to the steam generation unit

were replaced by flexible stainless steel tubes. The reactant gases from the cylinder are made to flow through the steel tubes to the mass flow controllers where their flow rates are accurately metered.

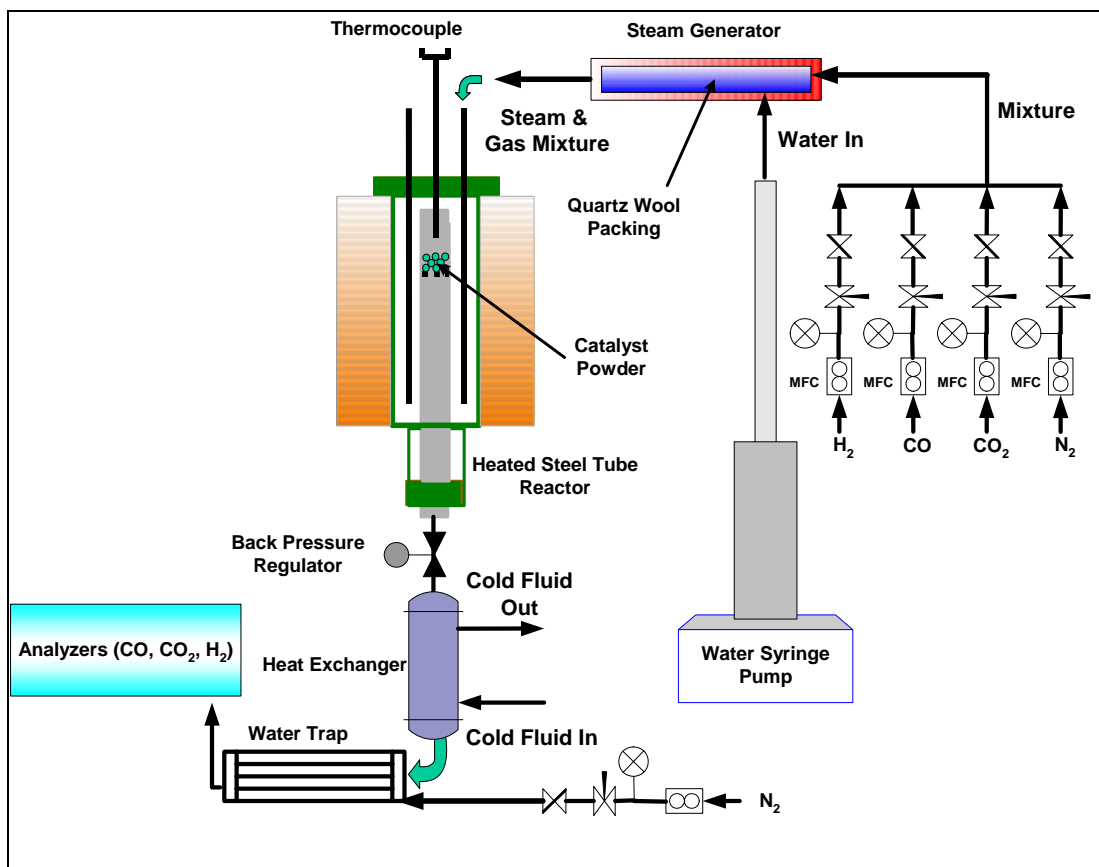


Figure 1: Modified integral fixed-bed reactor setup for conducting high pressure WGS and carbonation reactions

The mass flow controllers can handle a pressure of about 21 atms. From the mass flow controllers the reactant gases flow through a steel tube to the steam generating unit. The steam generating unit is maintained at a temperature of 200 °C and contains a packing of quartz chips which provide a large surface area of contact between the reactant gases and the water. The steam generating unit not only facilitates the complete evaporation on the water being pumped into the steam generating unit but it also serves to preheat the reactant gases entering the reactor. The reactor has been provided with a pressure gauge and a thermocouple to monitor the temperature and pressure within. The reactant gases leaving the reactor enter the back pressure regulator which builds pressure by regulating the flow rate of the gases flowing through it. The pressure regulator is very sensitive and the pressure within the

reactor can be changed quickly without any fluctuations by just turning the knob. The back pressure regulator is also capable of maintaining a constant pressure for a long period of time thereby increasing the accuracy of the experiments conducted.

Reactor Setup troubleshooting and shakedown

Initial problems were encountered during the catalyst and the catalyst and sorbent runs while conducting high pressure experiments. The pressure in the reactor could not be built beyond 100psig. Occasionally, in a few experiments huge fluctuations in the gas flow were also obtained. These problems were traced back to the same cause wherein the powder in the reactor rod was being blown out into reactor and into the tubes connected to the reactor. This was due to the backpressure developed in the reactor rod. The pressure could not be built in the reactor due to the sorbent powder clogging the orifice of the pressure regulator, preventing the regulator to be completely closed. Also, the powder that had entered the tube connecting the steam generating unit to the reactor began collecting there and reducing the cross section of the tube causing a huge localized pressure drop. This pressure drop caused the condensation of the steam entering the reactor which results in the formation of water droplets thereby leading to large fluctuations in the flow rate of the gases. This problem was solved by restricting the flow of the powder from the reactor tube by placing a small amount of quartz wool in the form of a thin layer over the powder bed. This method of preventing the entrainment of the powder along with regular cleaning and maintenance of the reactor solved both the problems mentioned above.

Modification of the setup to conduct ambient pressure H₂S experiments

Ambient pressure experiments were conducted to study the simultaneous removal of H₂S and CO₂ during hydrogen production in the same integral bed reactor as used before. An H₂S mass flow controller (15% H₂S) was procured from Brooks instruments (model 5850E) for accurately monitoring the flow of H₂S into the system. Also an H₂S analyzer model 921 was procured from Ametek instruments which can detect H₂S in the range of 0-1250ppm. The analyzer was integrated in the system upstream of the CO and CO₂ analyzer. Since H₂S is a toxic gas and cannot be directly sent to the vent an amine scrubbing system was installed downstream of the analyzers. The amine scrubbing system consisted of two tanks the first one left empty and the second one filled with a solution of mono ethanol amine through

which the gas was made to bubble. The first one was left empty to prevent the backflow of the amine solution into the analyzers.

High Pressure Water Gas Shift Reaction Testing

The water gas shift reaction was conducted using the high temperature shift (HTS) catalyst (iron oxide on chromia) obtained from Süd-Chemie. These experiments were conducted as base line experiments to determine the optimum conditions for maximum WGSR catalytic activity at different temperatures and pressures. Catalyst fines were used in a fixed bed reactor setup for all the experiments. The total flow rate of the gases through the reactor was maintained a constant at 725 sccm for all the experiments and the concentration of carbon monoxide in the reaction mixture was maintained at 10.3 %. 0.25 g of the catalyst was loaded into the reactor and the pressure, temperature and gas flow rates were adjusted for each run. The steam free gas compositions at the outlet of the reactor were monitored continuously using the CO, CO₂ and H₂ gas analyzer system described earlier (Annual Technical Progress Report, September 2005). The reactions were conducted at different temperatures ranging from 450 – 750°C, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0 - 300 psig.

Simultaneous WGS and carbonation at High Pressures

The combined water gas shift and carbonation reaction was conducted using the same experimental setup described earlier. A sorbent (calcium oxide) to catalyst ratio of 10:1 was used for all the experiments conducted. The combined water gas shift and carbonation reaction experiments were conducted at 600, 650, and 700°C with an S/C ratio of 3:1, 2:1, 1:1 at various pressures ranging from 0-300 psig. The PCC is calcined in-situ at 700 °C in a stream of nitrogen until the carbon dioxide analyzer confirms the absence of CO₂ in the outlet stream. The catalyst is then pretreated in an atmosphere of steam and hydrogen (1:1 ratio) to convert it to the magnetite phase (Fe₃O₄), which is the active form for the water gas shift reaction. The combined reaction is then performed at 650 °C in the presence of 10 % of CO. This being an unsteady state experiment the data collection is started exactly when the carbon monoxide and steam are started to flow into the reactor and the time taken for the gases to reach the analyzers is accounted for by the incorporation of the residence time calculation.

RESULTS AND DISCUSSIONS

WGS iron oxide catalyst deactivation, phase transformation, and pre-treatment,

It is imperative to understand the HTS catalyst composition through an iron oxide phase diagram (Figures 2 and 3). Iron oxide occurs in three different phases: Hematite (Fe_2O_3), Magnetite (Fe_3O_4) and Wustite (FeO). The active phase of the HTS catalyst is Magnetite (Fe_3O_4). However, in the presence of an oxidizing atmosphere, like pure CO_2 , the Magnetite phase gets oxidized to Hematite (Fe_2O_3). This is evident from the iron oxide phase diagram for CO - CO_2 system as illustrated in Figure 2. Thus, a pretreatment procedure was developed which reduces the oxidized form to the required phase. This step consists of treating the oxidized catalyst to a 20% H_2 in 80% H_2O stream at 600 °C which reduces the Hematite (Fe_2O_3) form to Magnetite (Fe_3O_4) form. This is clear from Figure 3. This fact was confirmed by X-ray diffraction analyses of the HTS catalyst before and after the pretreatment procedure. The HTS catalyst as obtained contains comprises of Fe_2O_3 (hematite) phase as shown in Figure 4 (a). The catalyst is subsequently subjected to the pretreatment procedure described earlier which changes its phase to the active magnetite (Fe_3O_4) form as shown in Figure 4 (b).

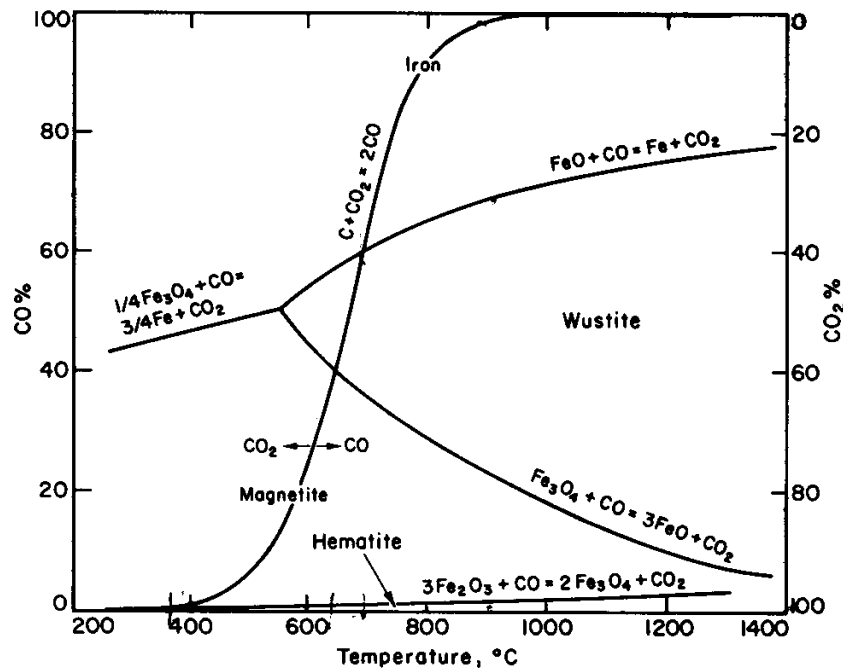


Figure 2: Equilibrium phase diagram for iron oxide system for various CO - CO_2 gas compositions and temperatures (adapted from Ross, 1980)

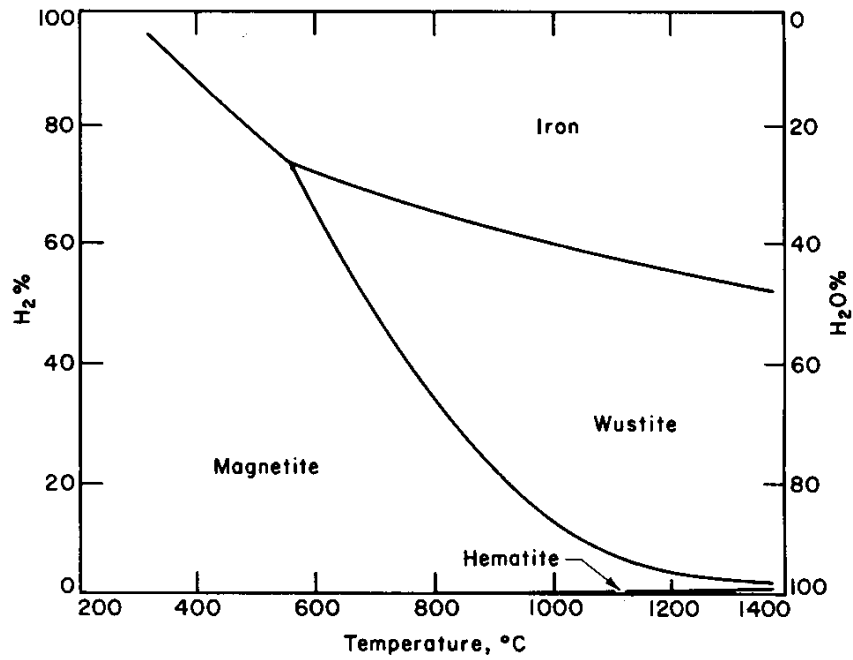
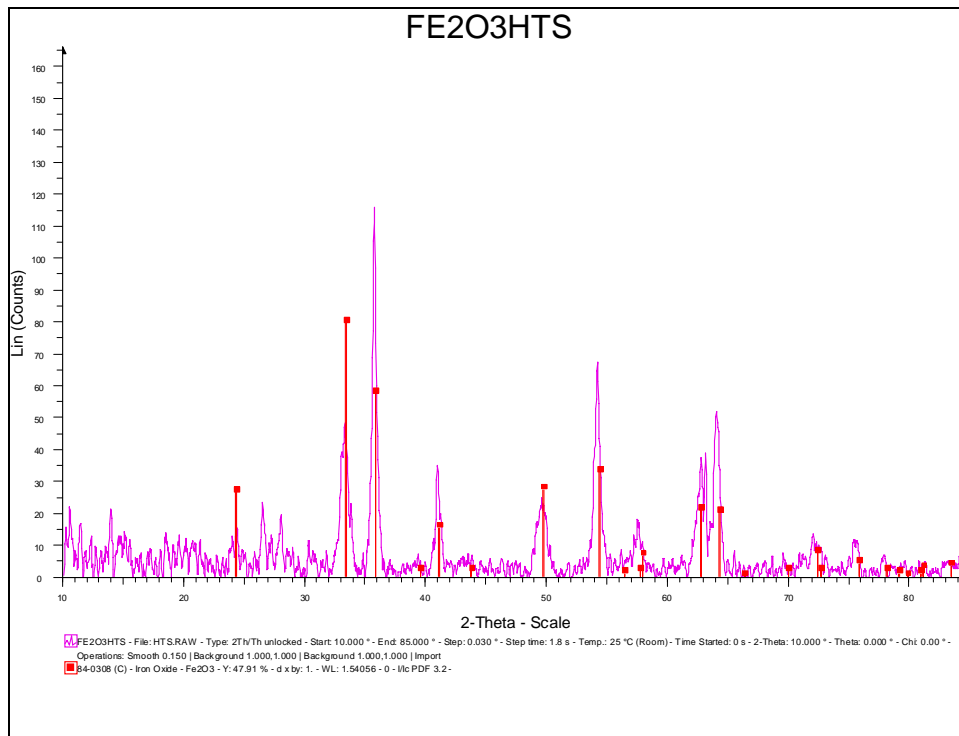
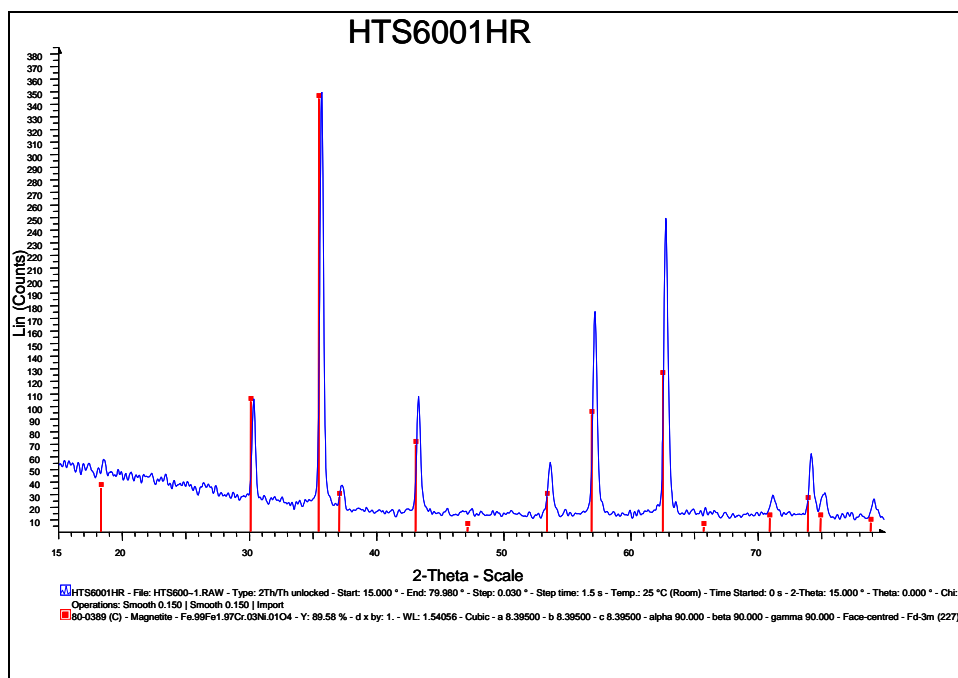


Figure 3: Equilibrium phase diagram for iron oxide systems for various H₂-H₂O gas compositions and temperatures (adapted from Ross, 1980)



(a) before pretreatment (hematite)



(b) after pretreatment (magnetite)

Figure 4: X-ray diffraction patterns of the high temperature shift (HTS) iron oxide catalyst

Combined WGS-carbonation reactions over multiple reaction-regeneration cycles, which include intermediate catalyst activation after every cycle, were performed using PCC-HTS system. Typically about 1.77 g of PCC-CaO was loaded in the reactor and the temperature was ramped to 700° in flowing N₂ to ensure the calcination of calcium carbonate to calcium oxide. After completion of the calcination, the reactor was cooled down to room temperature and 0.25 g of HTS catalyst was mixed into the reactor. The reaction temperature was then raised to 600°C and the catalyst pretreatment gas mixture consisting of a steam to H₂ ratio of 4:1 in N₂ for one hour. This pretreatment step activates the catalyst by reducing the HTS catalyst from Fe₂O₃ (hematite) to Fe₃O₄ (magnetite). The reaction gas mixture of 10.3% CO and 31% H₂O, and the balance being 5.0 grade N₂ was then sent into the reactor. The total gas flow-rate was maintained at 0.725 slpm and the steam/CO ratio was set at ~3. After the calcium oxide sorbent reaches its maximum loading capacity and the system reaches steady state and the reactor temperature was subsequently ramped to 700° C in flowing N₂ to effect the calcination of the carbonated sorbent. Subsequent to the calcination step the catalyst pretreatment is performed and the combined WGS-carbonation reaction is

then conducted in the flowing reaction gas mixture. Thus, the sequence of operation is (a) combined WGS-carbonation reaction, (b) catalyst pretreatment, (c) calcination. This three step procedure was repeated for five continuous cycles.

The details of the CO conversion breakthrough curve for all the 5 cycles are depicted in Figure 5. The system gives 100% conversion for 90 seconds through the first cycle and the sorbent reached its breakthrough loading at 1091 seconds (18.2 min). Beyond this the CO conversion of 80 % corresponds to that obtained with only the catalyst at 600° C. For the second reaction cycle the system gave almost 100% conversion for 64 seconds and the sorbent reached its breakthrough loading at 787 seconds (13.1 min). The final CO conversion for the second cycle was 80 %. The third reaction cycle resulted in almost 100% conversion for 79 seconds and the sorbent reached its breakthrough in 818 seconds. The final CO conversion for the third cycle was 78%. In the fourth cycle the system did not achieve 100% CO conversion and the sorbent reached its breakthrough in 891 seconds. The final CO conversion for the fourth cycle was 69%. The fifth reaction cycle also did not result in 100% CO conversion and the time for the sorbent to reach its maximum loading capacity was 719 seconds. The final CO conversion for the fifth cycle was 69%. Thus the final steady state CO conversion of the system, after it has reached the breakthrough, varies from 80% to 69% over five cycles. This depicts a drop in the catalyst activity of only 11% while the catalyst is exposed to 5 cycles. This is in sharp contrast to the significant drop in the catalyst activity when the catalyst pretreatment was not conducted. This can be observed by the drop in the catalytic activity from 80% in the first cycle to 40% in the second cycle as illustrated in Figure 5. Thus, the intermediate catalyst pretreatment helps prevent catalyst deactivation by reducing the catalyst to its active magnetite (Fe_3O_4) form.

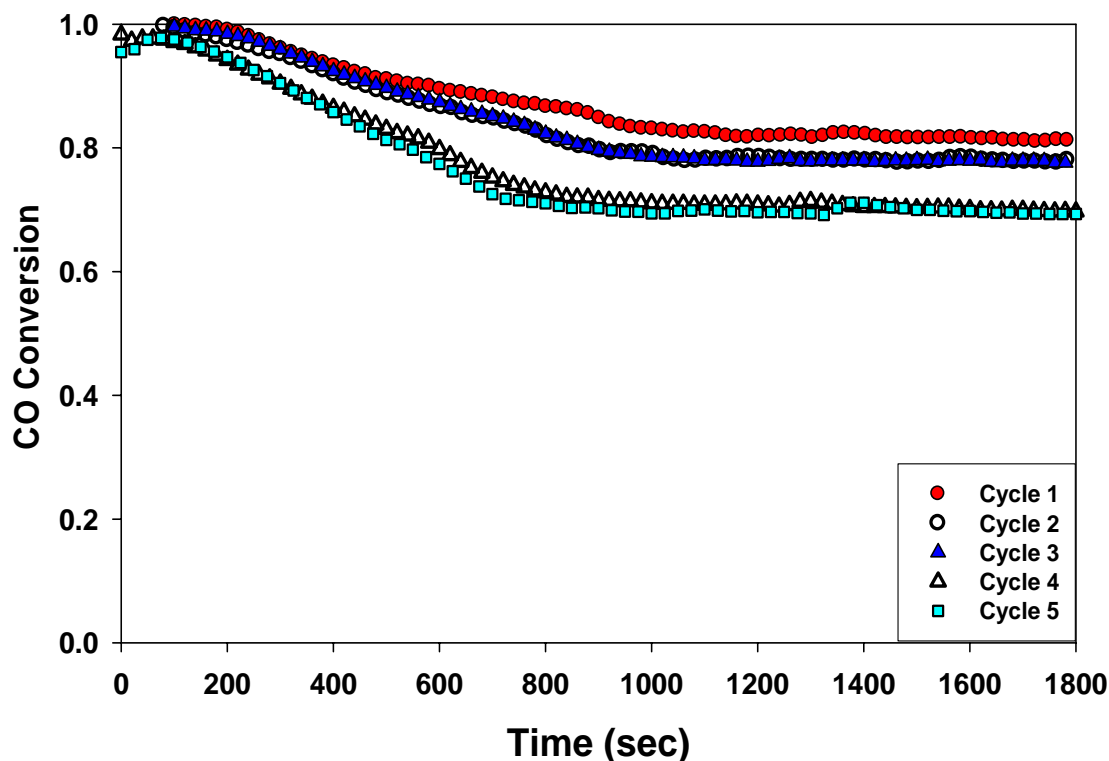


Figure 5: Breakthrough curve depicting the CO conversion for PCC-HTS catalyst system for five cycles ($T = 600\text{ }^{\circ}\text{C}$, 10.3% CO, 31% H_2O , Total flow = 0.725 slpm)

High Pressure Water Gas Shift Reaction Testing

Figure 1 shows the CO conversion profiles for increasing reaction temperatures as well as the S/C ratios at ambient pressures. The CO conversion increases with increasing temperature up to a critical temperature (550-650 $^{\circ}\text{C}$) beyond which it begins decreasing monotonically. It can be seen from Figure 1 that at 0 psig and a S/C ratio of 3: 1 the conversion increases from 45.8 % at 450C to 83.2 % at 600 $^{\circ}\text{C}$. It is well known that the rate of the reaction increases as temperature increases. Beyond 600 $^{\circ}\text{C}$ the conversion decreases and at 800 C it is 69.4%. This is observed due to the opposing trends of the reaction kinetics and thermodynamic equilibrium with increasing temperature. As the temperature increases the reaction rate increases while the equilibrium constant decreases. Thus at lower temperatures although the equilibrium constant is high the reaction rate is very low and at high temperatures the reaction is very fast but the equilibrium constant is very low. Consequently maximum conversion is reached at an optimum temperature at which both the kinetics and the reaction equilibrium are favorable. From Figure 1 it can be seen that the conversion increases with an increase in the S/C ratio. At a temperature of 650 $^{\circ}\text{C}$ the conversion is 63.5% for a S/C ratio

of 1:1 while it is 71.6% for 2:1 and 80.28% for 3:1. This is in accordance with the Le Chatelier's principle where, as the reactant composition increases the equilibrium will be shifted in the forward direction and will favor the formation of the products. It can also be seen from Figure 6 that as the S/C ratio increases the temperature at which maximum conversion is reached decreases. While for 1:1 the maximum conversion is reached at 650°C for 3:1 it is reached at 550°C. This can be explained based on the previous trends. As the steam concentration is increased the equilibrium is shifted in the forward direction and hence the maximum conversion that can be obtained according to thermodynamics is achieved at a lower temperature. As the temperature increases beyond this point the conversion remains almost the same until thermodynamics dictates a lowering in the conversion at high temperatures.

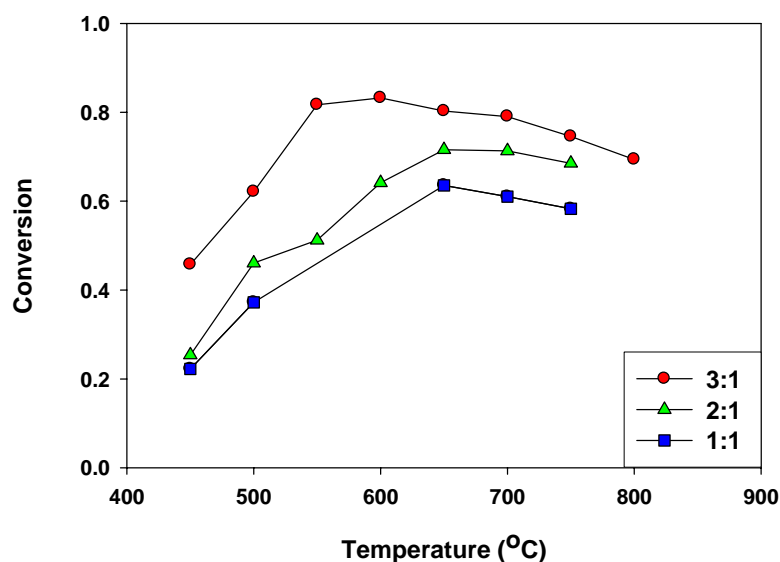


Figure 6: Effect of reaction temperature on CO conversions for various steam: CO ratios at 0 psig (0.25g HTS, Total flow = 0.725 slpm)

The water gas shift reaction conducted at 150 psig follows the same trend as the 0 psig experiments as evident from Figure 7 below. The CO conversion trend shows the presence of an optimal value for varying temperature. For a steam: CO ratio of 1:1 the conversion is 46.2 % at 450C reaches a maximum at 550 C with a conversion of 69.2 % and then decreases to 62.7 % at 650°C. At 550C a conversion of 69.2 % is reached for a S/C ratio of 1:1, 84.2 % for 2:1, and 86.3% for 3:1. On comparing Figure 6 with Figure 7 it is evident that at any temperature the conversion is always higher at 150 psig when compared to 0 psig. Also the

curves for conversion are flatter at 150 psig when compared to 0 psig, which shows that the temperature dependence on the conversion decreases with an increase in the pressure.

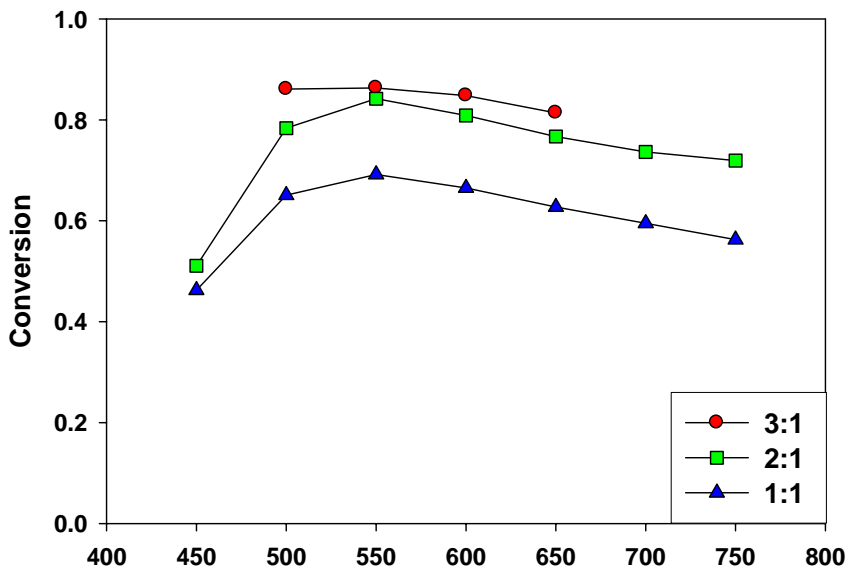


Figure 7: Effect of reaction temperature on CO conversions for various steam: CO ratios at 150 psig (0.25g HTS, Total flow = 0.725 slpm)

The effect of reaction temperatures and S/C ratios on CO conversion at 300 psig follows exactly the same trend as that for 150 psig and 0 psig. In addition, at any temperature the conversion at 300 psig is always greater than at 150 psig or 0 psig. For a temperature range of 450 C to 750 C the conversion varies over a smaller range for 300 psig when compared to either 150 psig or 0 psig showing that the dependence of conversion on temperature decreases with an increase in the total reaction pressure.

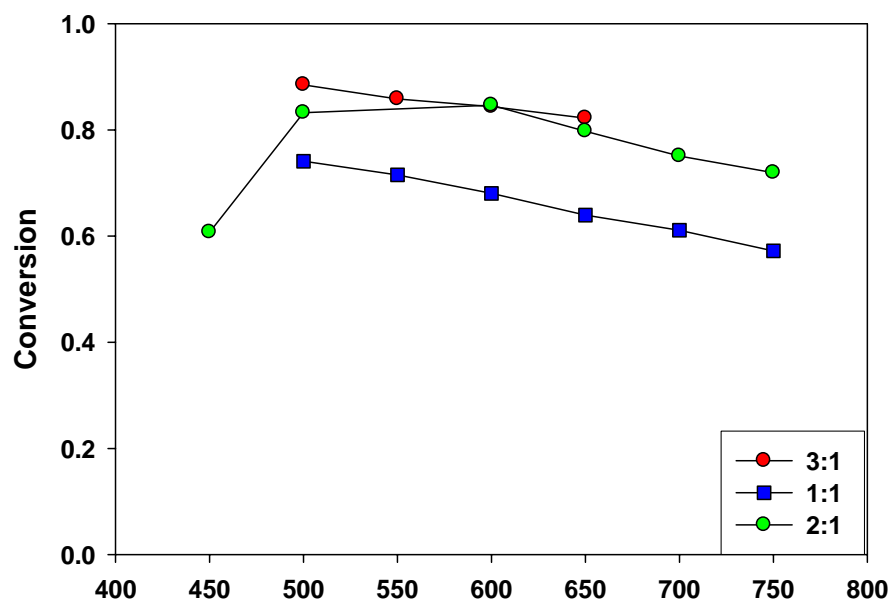


Figure 8: Effect of reaction temperature on CO conversions for various steam: CO ratios at 300 psig (0.25g HTS, Total flow = 0.725 slpm)

From Figure 9 it can be seen that for a S/C ratio of 1:1, the conversion increases with an increase in the pressure. At 500°C the conversion is 0.3890 for 0 psig, 0.6506 for 150 psig and 0.7411 for 300 psig. As the total pressure increases there is an increase in the partial pressure of the reactants that results in an increase in the overall rate of the reaction. From Figure 9 it can also be seen that the maximum conversion is reached at lower temperatures as the pressure increases. At 0 psig 600°C gives the maximum conversion, at 150 psig 550°C gives maximum conversion and at 300 psig a temperature lower than 500 C gives maximum conversion. This is because as the pressure increases the rate of the reaction increases and hence maximum conversion is reached at lower temperatures.

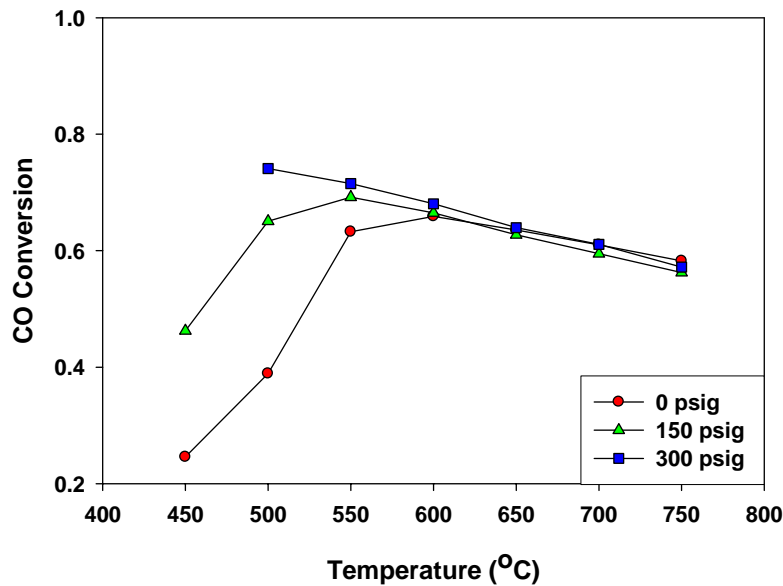


Figure 9: Effect of reaction temperature on CO conversions for various pressures (S/C ratio = 1:1; Total flow = 0.725 slpm)

When a steam to CO ratio of 2:1 is used the conversion with respect to temperature and pressure varies in a manner similar to a steam to CO ratio of 1:1. On comparing the Figure 5 and Figure 6 it can be seen that for all temperatures the conversion is always higher for a steam to CO ratio of 2:1. At 0 psig maximum conversion is achieved at a temperature of 650 C while at 300 psig it is achieved at a temperature of 550°C.

When a S/C ratio of 3:1 is used the conversion with respect to temperature and pressure varies similar to earlier cases of 1:1 and 2:1. On comparing Figures 9-11 it can be seen that for all temperatures the CO conversion is always higher for a S/C ratio of 3:1. At 0 psig maximum conversion is achieved at a temperature of 600° C while at 150 psig it is achieved at a temperature of 550°C and at 300 psig it is at a temperature lower than 500°C.

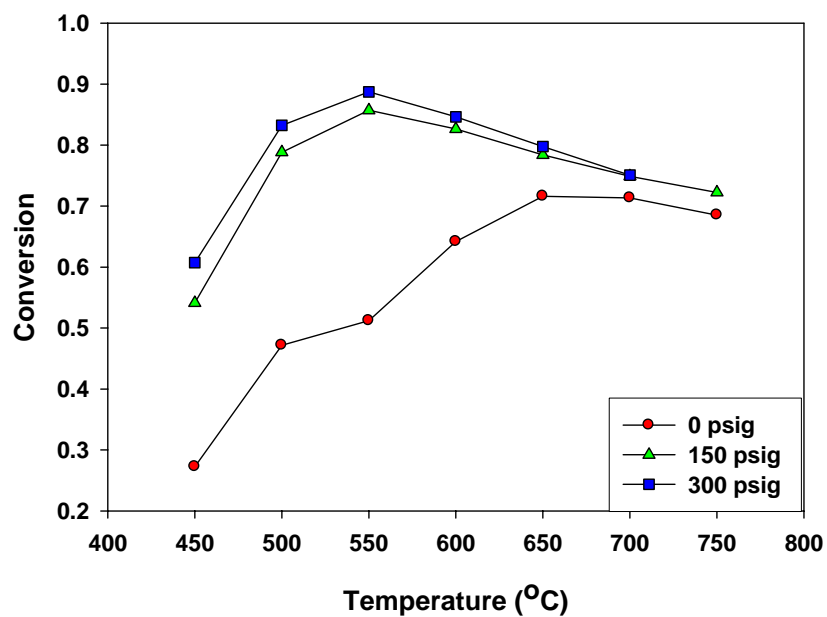


Figure 10: Effect of reaction temperature on CO conversions for various pressures (S/C ratio = 2:1; Total flow = 0.725 slpm)

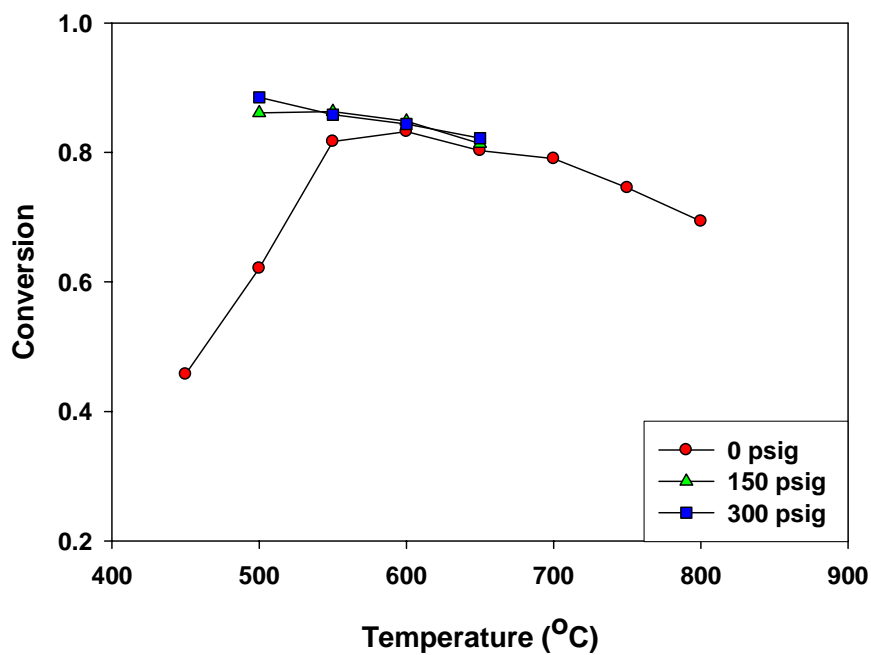


Figure 11: Effect of reaction temperature on CO conversions for various pressures (S/C ratio = 3:1; Total flow = 0.725 slpm)

Figure 12 depicts the variation in the optimal reaction temperature for maximum CO conversion with increasing total pressure and S/C ratio. It can be seen that maximum conversion is achieved at lower temperatures as the pressure increases. For a S/C ratio of 3:1, at a pressure of 0 psig maximum conversion is achieved at 600C while at 300 psig it is 500 C. This is due to the fact that with increase in the total pressure there is an increase in the rate of reaction and hence higher conversion can be achieved at lower temperatures. Besides, at lower pressures increasing the S/C ratio reduces the optimal temperature for maximum CO conversion. At higher pressures the S/C ratio does not affect the optimal reaction temperature that remains the same for all the ratios.

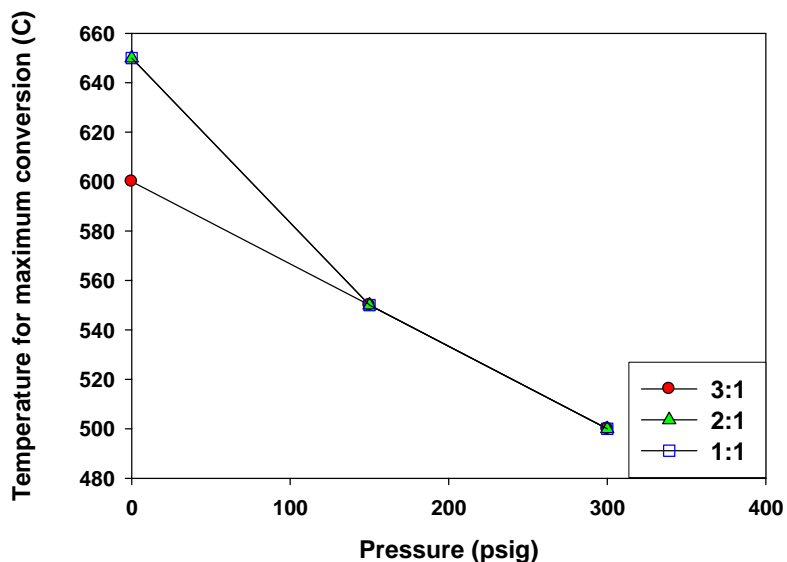


Figure 12: Variation in the optimal temperature with respect to pressure at various S/C ratios

The partial pressure ratios of the products to the reactants were computed for each case of S/C ratio and were compared with the equilibrium values obtained from HSC Chemistry v 5.0 (Outokumpu Research Oy, Finland). The observed partial pressure ratio (K_{obs}) was computed from the experimental data by obtaining the ratio of the partial pressures of the products and the reactants as per the eqn given below:

$$K_{obs} = \frac{P_{H_2} P_{CO_2}}{P_{CO} P_{H_2O}}$$

As shown in Figures 13-15 it was found that each of these values of the observed ratios (K_{obs}) was within the theoretical equilibrium value predicted by thermodynamics. From

Figure 13 it can be seen that for a S/C ratio of 1:1 the partial pressure ratio increases with an increase in the temperature till it approaches equilibrium and then decreases along the equilibrium curve. Besides, as the pressure increases the curves for the partial pressure ratios approach equilibrium more closely and this can be explained by the increase in the rate of the reaction at higher pressures.

From Figures 14-15 it is observed that when S/C ratios of 2:1 and 3:1 are used the exact same trend is observed. A comparison of Figures 13-15 yields that with an increase in the S/C ratios the system moves away from equilibrium. This is justified as an increase in one of the reactants will lead to a lowering in the partial pressure ratio (K_{obs}) and hence the deviation from equilibrium.

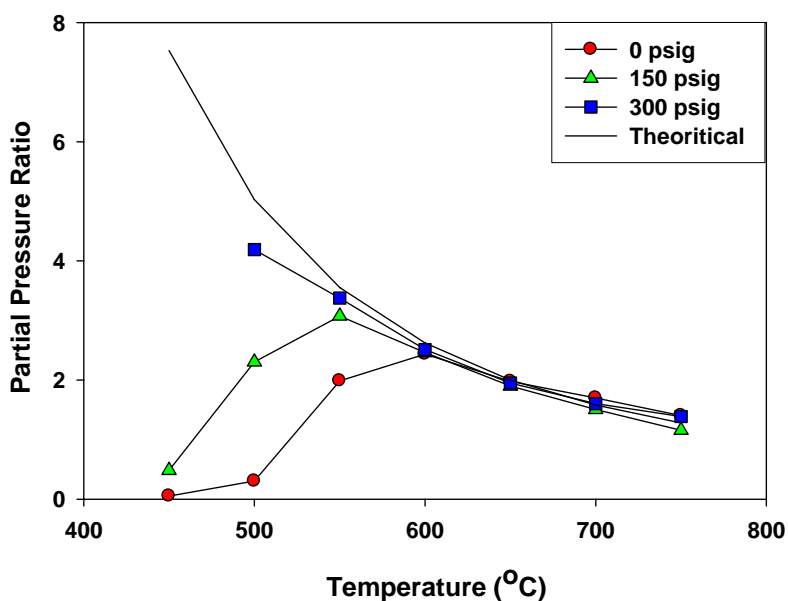


Figure 13: Effect of temperature on the partial pressure ratio of the products to the reactants for various pressures (S/C ratio = 1:1; Total flow = 0.725 slpm)

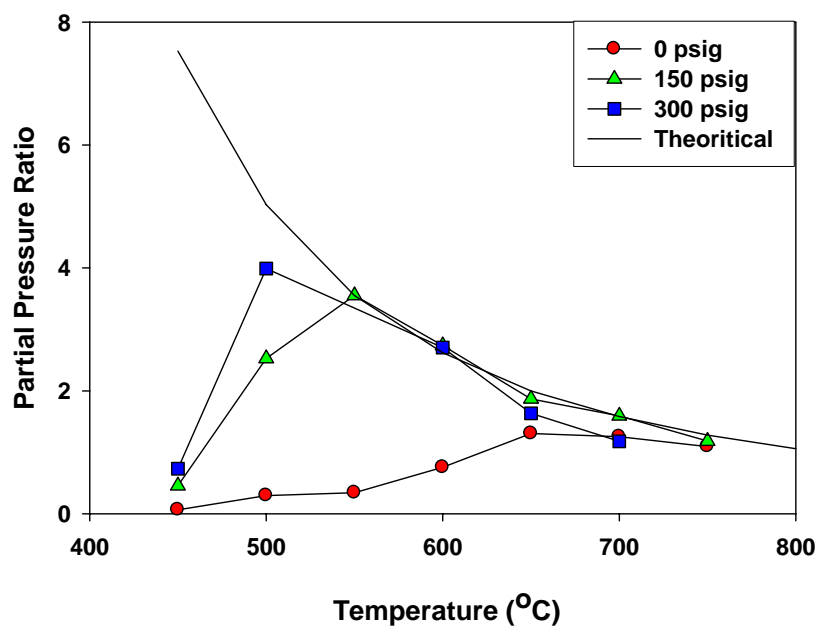


Figure 14: Effect of temperature on the partial pressure ratio of the products to the reactants for various pressures (S/C ratio = 2:1; Total flow = 0.725 slpm)

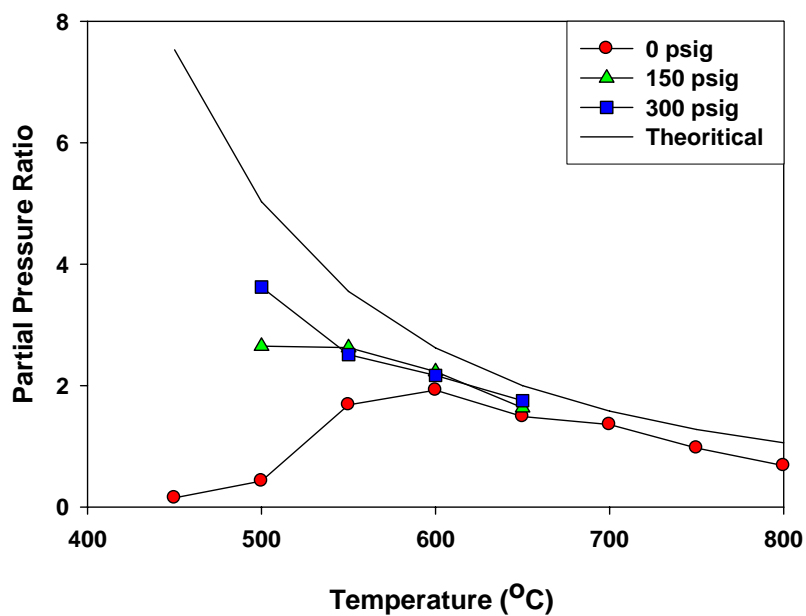


Figure 15: Effect of temperature on the partial pressure ratio of the products to the reactants for various pressures (S/C ratio = 3:1; Total flow = 0.725 slpm)

Determination of the residence of the gases through the reactor setup

The residence time of the gases through the entire reactor setup was determined for three different pressures of 0 psig, 150 psig and 300 psig. The residence time was determined by monitoring the time required for the gases to reach the analyzers. This was obtained by flowing CO through the reactor and measuring the time taken for it to reach the analyzer. This test was done at all three pressures. For 0 psig, the residence time was found to be 107 secs, for 150psig it was 300 secs and for 300 psig it was 470 secs. This residence time calculation is very essential while analyzing the data for unsteady state runs in the presence of the sorbent. This residence time for the gases is subtracted from the continuous data obtained through the analyzer based system to give the actual conversion and gas composition data.

Simultaneous WGS and Carbonation at High Pressures

Figures 16-18 illustrate the breakthrough curves for CO conversions with varying total pressure (0-300 psig) and a S/C ratio of 3:1. From Figure 16 it can be seen that at 0 psig a maximum conversion of 96% is obtained for the first 265 seconds after which there is a drop in the conversion due to the consumption of the sorbent which constitutes the breakthrough region of the curve and finally the conversion drops down to about 80% which determines the steady state catalytic activity. From Figure 17 it can be seen that at 150 psig a maximum conversion of 99.78% is obtained for the first 1168 seconds. During this initial pre break through phase both the carbonation and the water gas shift reaction are active and hence the conversion obtained is very high. During the breakthrough phase the conversion for the carbonation reaction decreases due to the progressing consumption of the sorbent which leads to a decrease in the conversion for the water gas shift reaction. In the post break through phase the sorbent has been completely consumed and hence the CO conversion is solely due to the water gas shift reaction. As seen in Figure 18 at 300 psig a maximum conversion of 99.88% is obtained for the first 1477 seconds after which the conversion in the post break through region remains steady at 86%.

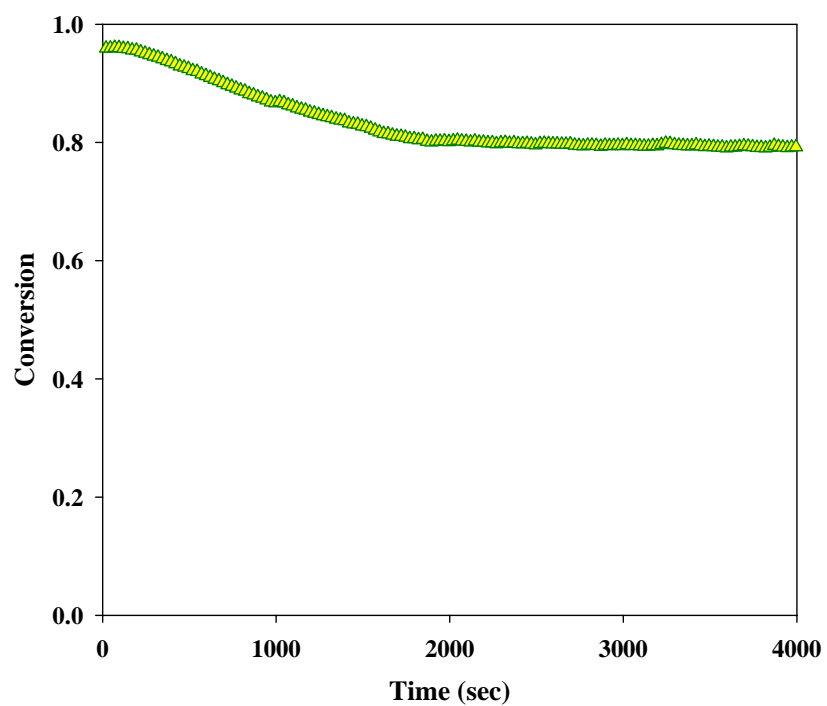


Figure 16: Break through curve for CO conversion at 650C, 0psig and S/C ratio=3:1

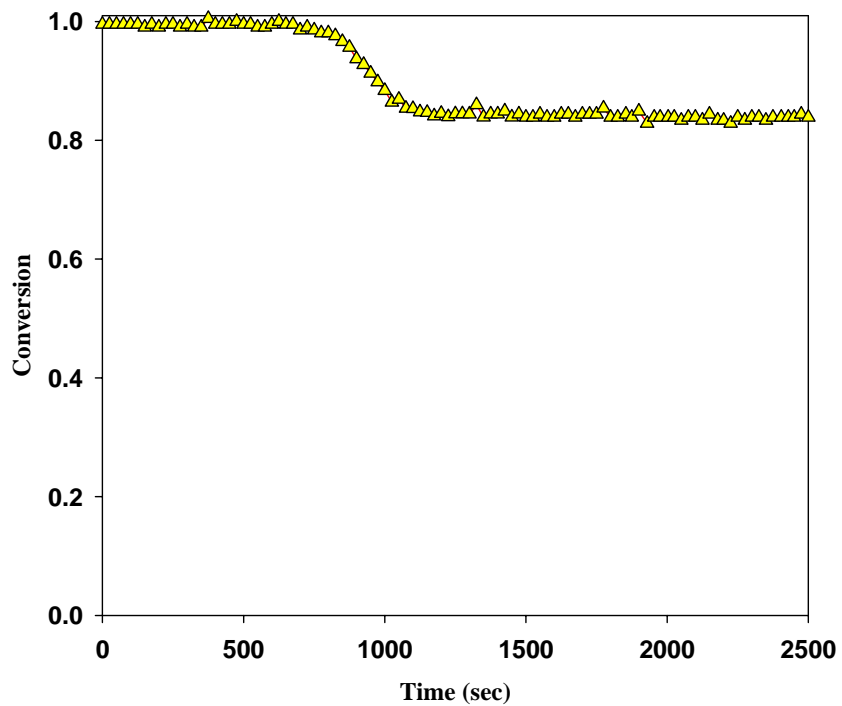


Figure 17: Break through curve for CO conversion at 650C, 150 psig and S/C ratio=3:1

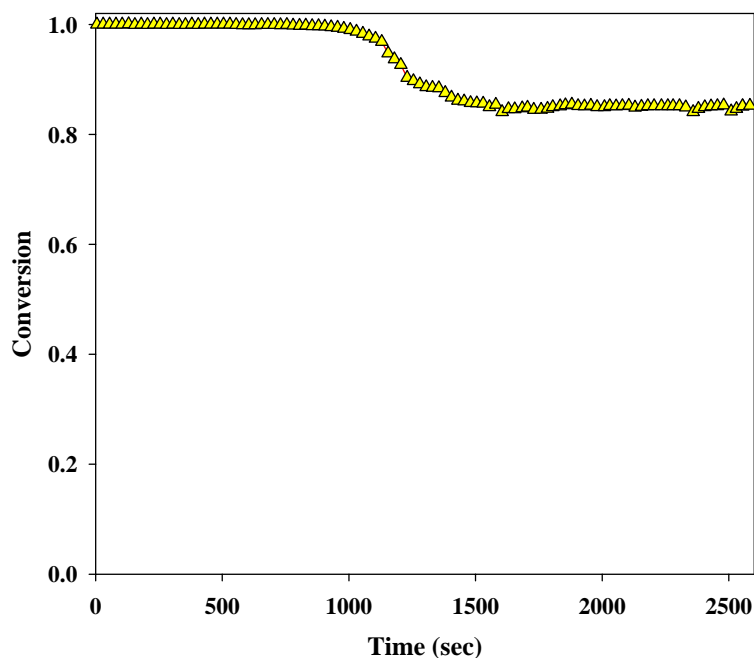


Figure 18: Break through curve for CO conversion at 650C, 300 psig and S/C ratio=3:1

Figure 19 compares the H₂ gas production breakthrough curves for increasing pressures at 650°C and S/C ratio of 3:1. From Figure 19 it can be seen that the H₂ gas purity obtained from the outlet of reactor increases with an increase in the total pressure. At 0 psig a 95.6 % hydrogen stream is produced while at 150 psig 99.7% pure hydrogen stream is obtained for the first 1168 seconds and at 300 psig a 99.8% pure hydrogen stream is produced for the first 1477 seconds.

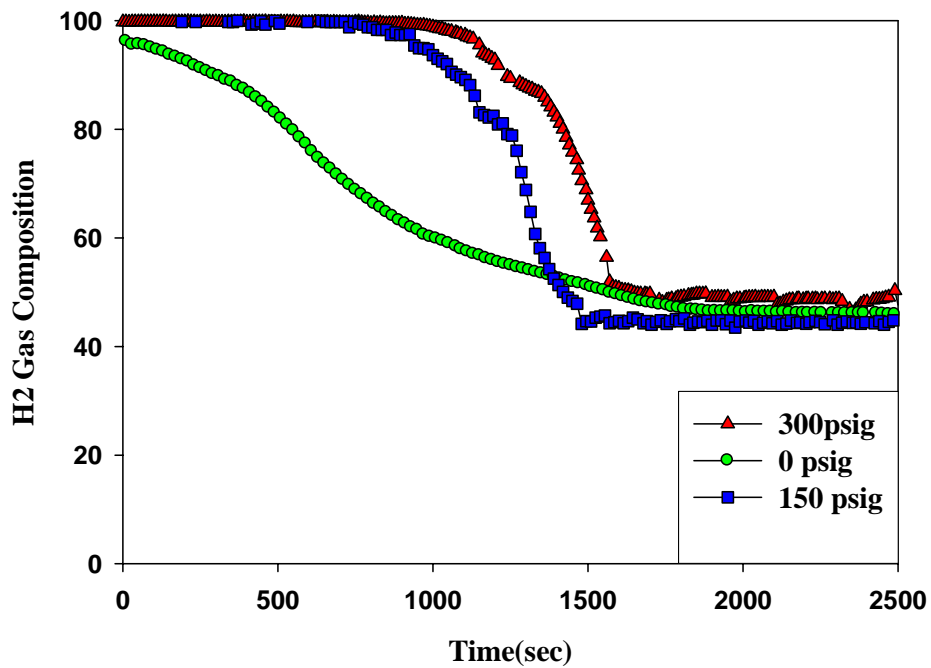


Figure 19: Effect of pressure of the hydrogen gas composition (Temperature=650°C, S/C ratio=3:1)

Figure 20 illustrates the fact that the time for which a pure H₂ stream is produced increases with an increase in the pressure. At 150 psig pure hydrogen is produced for 1167 seconds while at 300 psig pure hydrogen is produced for 1477 seconds. It can also be seen from the curve that an increase in the pressure from 0 to 150 psig results in a steeper increase in the time for which pure hydrogen is produced than when the pressure is increased for 150 psig to 300 psig. Hence it is evident that any further increase in the pressure will increase the time of pure hydrogen production by only a small amount.

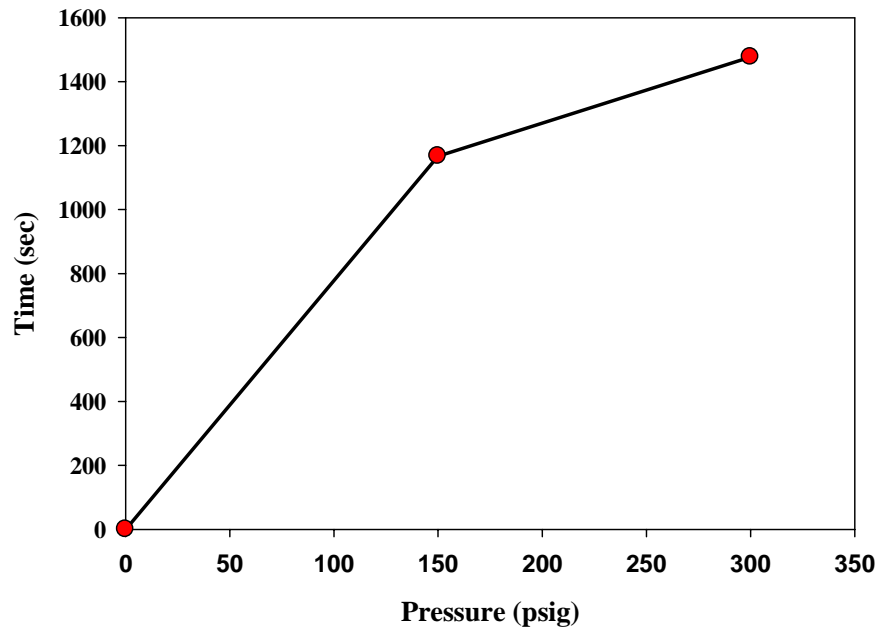


Figure 20: Effect of pressure on the time for which hydrogen production approached 100% purity

The combined water gas shift and carbonation reactions were conducted at various temperatures to determine the effect of temperature on the kinetics of the reaction and to determine the suitable operating temperature range for the combined reactions. The effect of pressure on the combined reaction was also investigated to determine the optimum pressure required for the production of high purity hydrogen. The main objective of this study is to determine the operating conditions for the production of high purity hydrogen while reducing the steam composition in the system.

From Figure 21 it can be seen that at 0 psig and 650 C with the decrease in the S/C ratio the hydrogen purity also decreases. In the pre breakthrough region of the curve while for an S/C ratio of 3:1, a 96 % hydrogen stream is produced, for an S/C ratio of 1:1; a 90% hydrogen stream is produced.

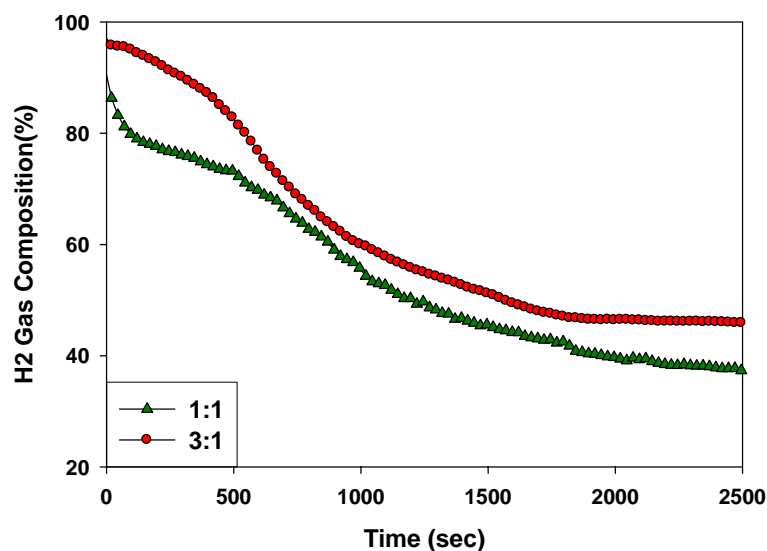


Figure 21: Effect of S/C ratio on the hydrogen gas composition (Temperature=650°C, Pressure = 0 psig)

When the combined water gas shift and carbonation reactions are conducted at a higher pressure of 150 psig the rate of the combined reactions is increased such that even at stoichiometric steam addition a hydrogen purity of close to 100% is obtained. From Figure 22 it can be seen that for an S/C ratio of 3:1 pure hydrogen is produced for 800 sec while for an S/C ratio of 1:1 it is produced for 450 seconds. As shown in Figure 23 for a pressure of 300 psig pure hydrogen is produced for the first 1000 seconds for an S/C ratio of 3:1 and for the first 900 seconds for an S/C ratio of 2:1. From the results obtained at high pressures it can be inferred that as the pressure is increased the time and purity of the hydrogen produced for smaller S/C ratios becomes closer to that produced for larger S/C ratios. Hence operating at high pressures will result in the production of high purity hydrogen even when the amount of steam in the system is reduced.

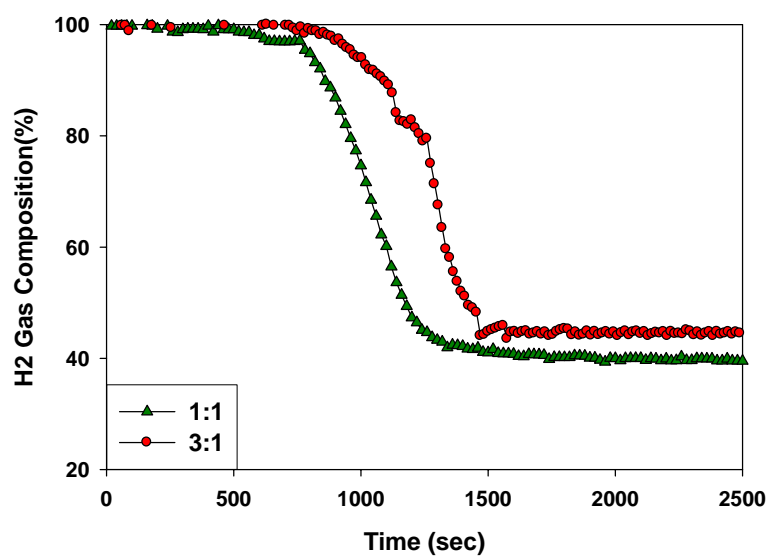


Figure 22: Effect of S/C ratio on the hydrogen gas composition (Temperature=650°C, Pressure =150 psig)

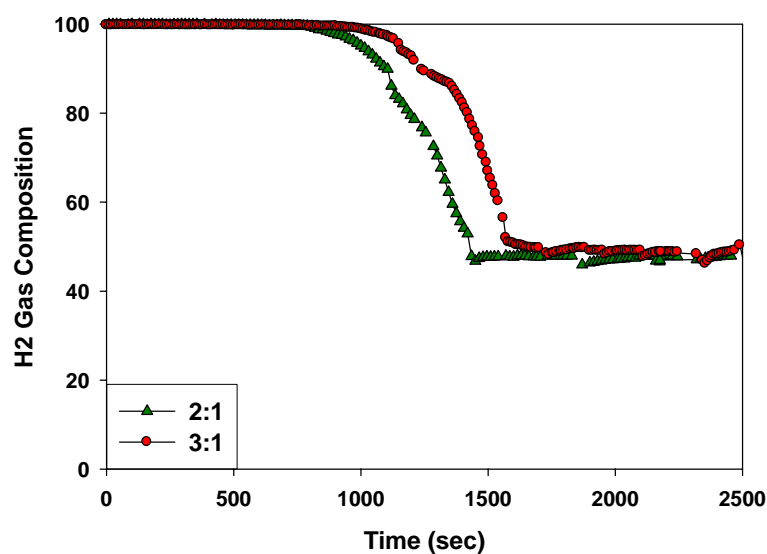


Figure 23: Effect of S/C ratio on the hydrogen gas composition (Temperature=650°C, Pressure = 300 psig)

Figure 24 shows the change in the hydrogen composition with respect to time at two steam to CO (S/C) ratios of 3:1 and 1:1 at 600 °C and 0 psig. It can be seen that with the increase in steam composition the purity of hydrogen produced also increases. While for an S/C ratio of 1:1 a 90 % hydrogen stream is produced, for an S/C ratio of 3:1 a 96 % hydrogen stream is produced. In addition, at a temperature of 600C and an S/C ratio of 3:1 the hydrogen

percentage is 96% in the beginning due to the combined water gas shift and carbonation reaction and it decreases to 40% after 1200 sec and this corresponds to the hydrogen produced by the water gas shift reaction only. At 650 C for the same temperature, pressure and S/C ratio the hydrogen purity is 96% in the beginning and it decreases to 48% in 1700 seconds. Comparing the results obtained at the two temperatures it can be seen that for an S/C ratio of 3:1 although the rate of carbonation at 600C is as good as that at 650C the rate of the water gas shift reaction is very low. It can be inferred from this that during the pre breakthrough period of the curve since the rate of the WGSR is lower at 600C than 650C the carbonation reaction at 600C has to be much better than at 650C in order to give the same purity of hydrogen.

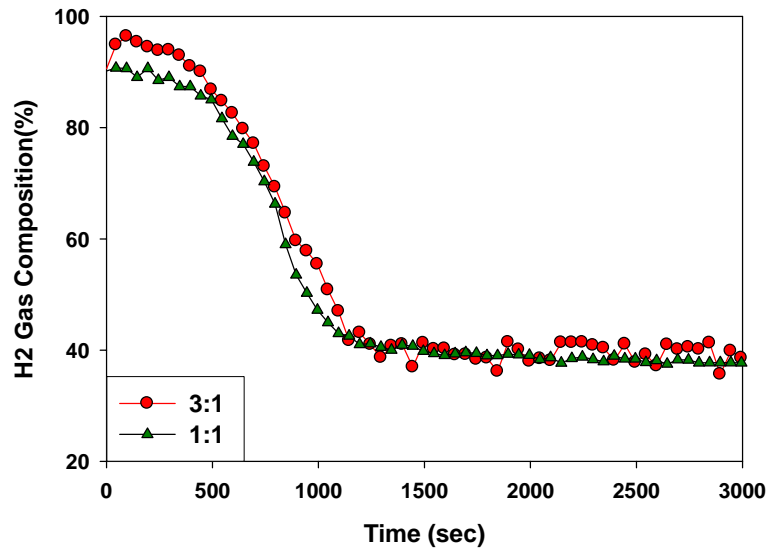


Figure 24: Effect of S/C ratio on the hydrogen gas composition (Temperature=600°C, Pressure = 0 psig)

At 600C, on increasing the pressure the combined water gas shift and carbonation reaction exhibits the same trend as that at 650 C. At 150 psig and an S/C ratio of 3:1 pure hydrogen was produced for 1000 secs. On decreasing the S/C ratio to 1:1 at 150 psig pure hydrogen was produced for 800 secs as shown in Figure 25. On increasing the pressure to 300 psig pure hydrogen is produced for 1400 secs for both S/C ratios of 3:1 and 1:1 as shown in Figure 26. Hence at 600 C, at high pressures the rate of the carbonation reaction is very high and the reduction in the steam addition does not alter the purity of the hydrogen produced. When the

sorbent gets consumed the carbonation reaction does not occur and on reducing the steam content from an S/C ratio to 3:1 to 1:1 the purity of the hydrogen reduces by 5%.

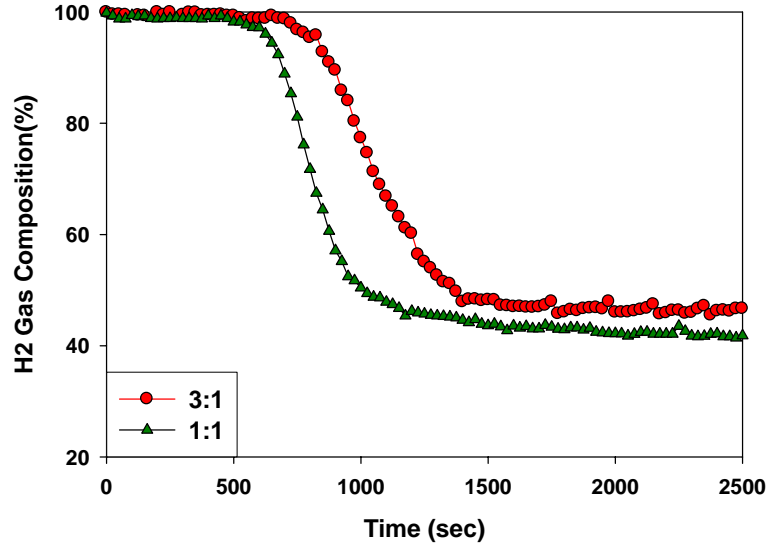


Figure 25: Effect of S/C ratio on the hydrogen gas composition (Temperature=600°C, Pressure = 150 psig)

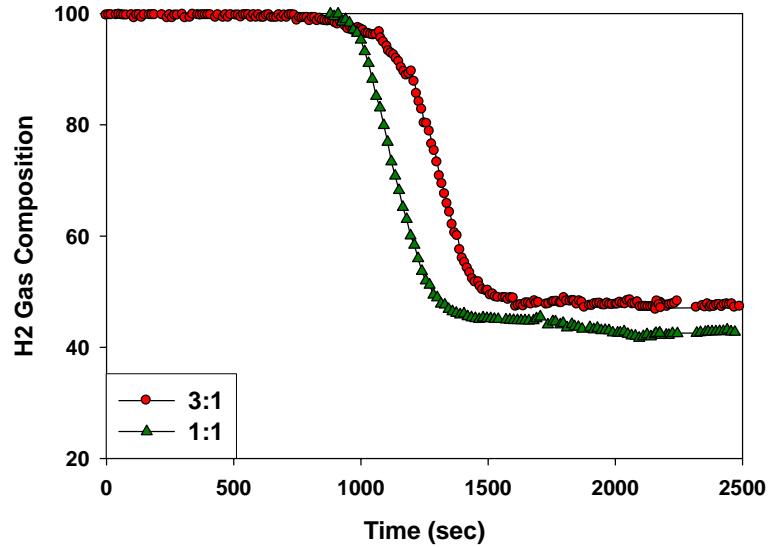


Figure 26: Effect of S/C ratio on the hydrogen gas composition (Temperature=600°C, Pressure = 300 psig)

Similarly Figures 27, 28 and 29 depict the hydrogen purity obtained by the combined water gas shift and carbonation reaction at 700C with different S/C ratios and at different pressures. The hydrogen purity was found to increase with increase in the S/C ratio and total pressure.

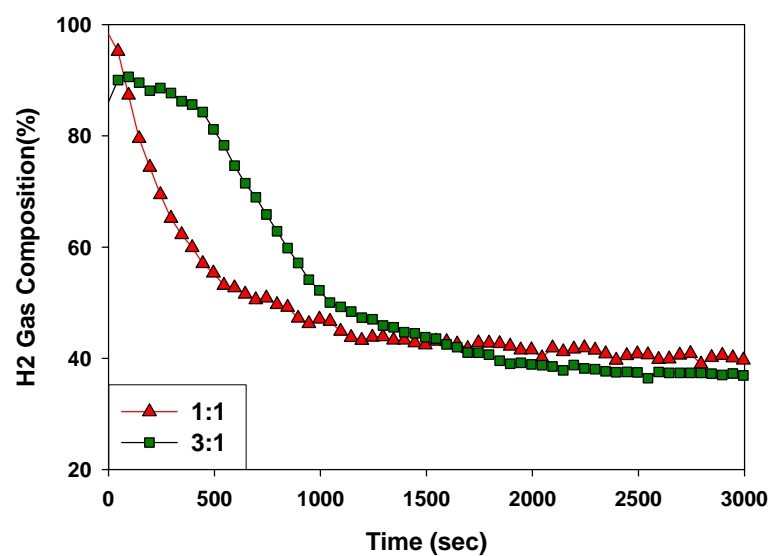


Figure 27: Effect of S/C ratio on the hydrogen gas composition (Temperature=700°C, Pressure = 0 psig)

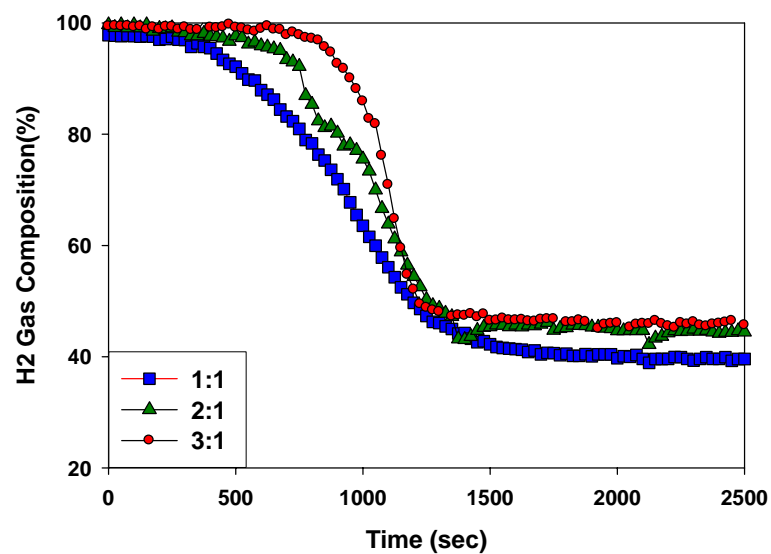


Figure 28: Effect of S/C ratio on the hydrogen gas composition (Temperature=700°C, Pressure = 150 psig)

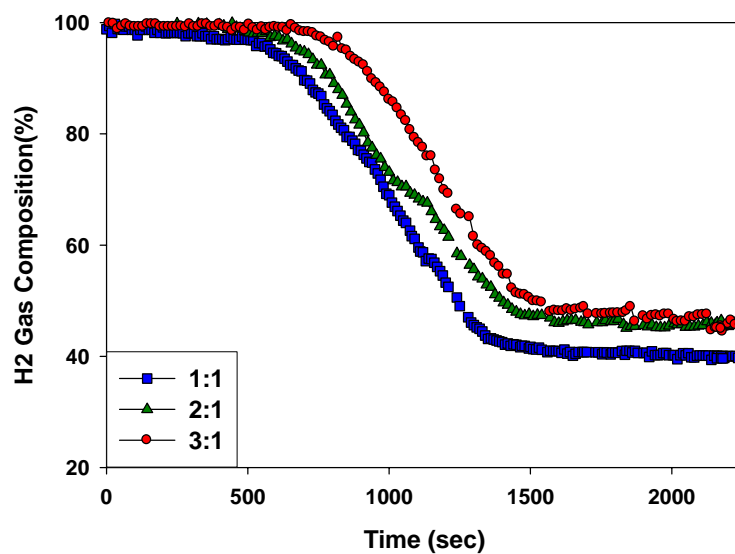


Figure 29: Effect of S/C ratio on the hydrogen gas composition (Temperature=700°C, Pressure = 300 psig)

Figures 30, 31, and 32 describe the CO conversion obtained at various temperatures at ambient pressure. It can be seen that at 0 psig the conversion in the pre breakthrough curve is higher at 600C and decreases with an increase in the temperature while the post breakthrough conversion increases with the increase in temperature and is highest at 700C.

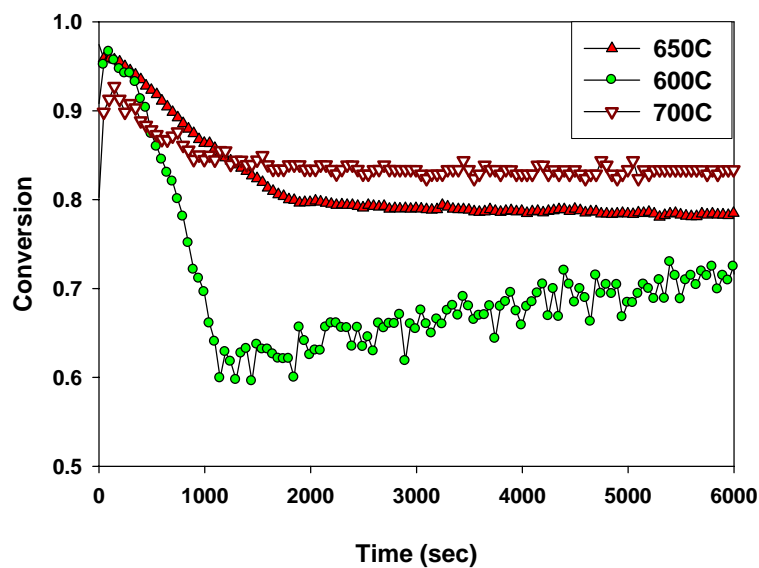


Figure 30: Effect of temperature on the CO conversion (S/C ratio= 3:1, Pressure = 0 psig)

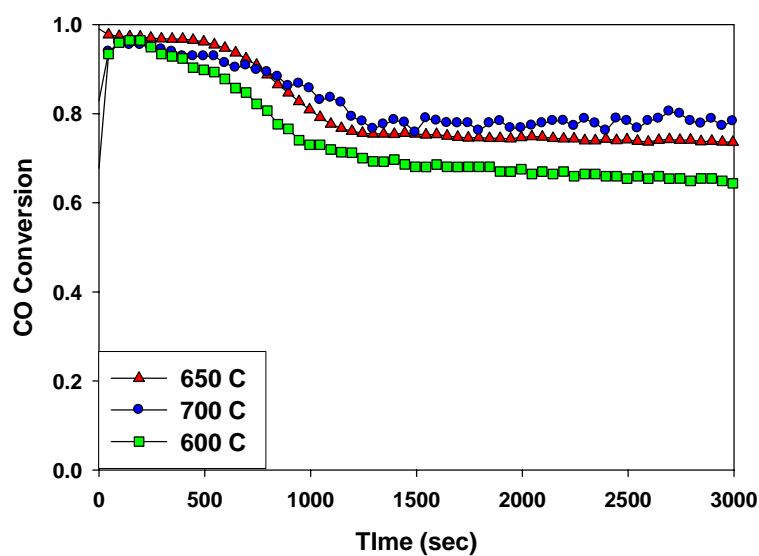


Figure 31: Effect of temperature on the CO conversion (S/C ratio= 2:1, Pressure = 0 psig)

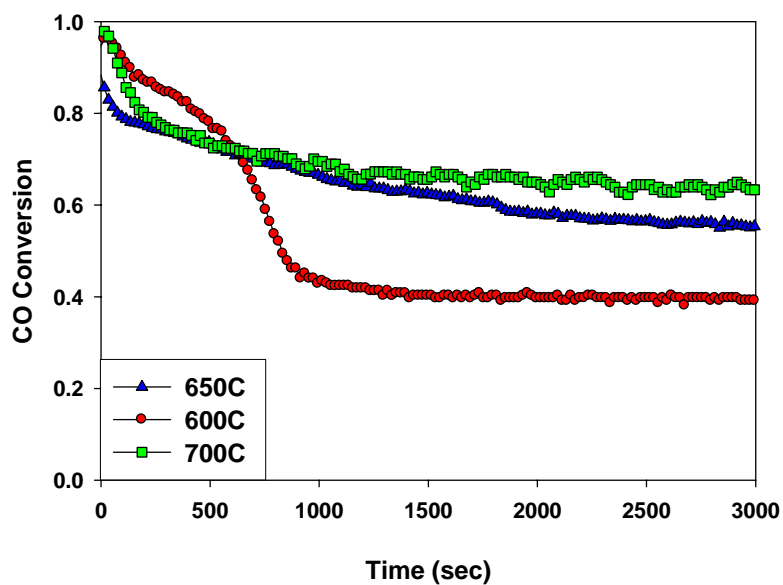


Figure 32: Effect of temperature on the CO conversion (S/C ratio= 1:1, Pressure = 0 psig)

As the pressure is increased the rate of both the carbonation and water gas reaction increase and highest conversion is achieved at lower temperatures in both the pre breakthrough and post breakthrough regions of the curve.

On comparing the CO conversion obtained at various temperatures for a pressure of 300 psig it was found that there is almost no difference in the CO conversion for an S/C ratio of 3:1 as can be seen in Figure 33. On decreasing the S/C ratio temperature begins to play an important role in the extent of CO conversion. As shown in Figure 34 and 35 as the S/C ratio is decreased, reducing the temperature improves the CO conversion and it is highest at 600C for every operating pressure.

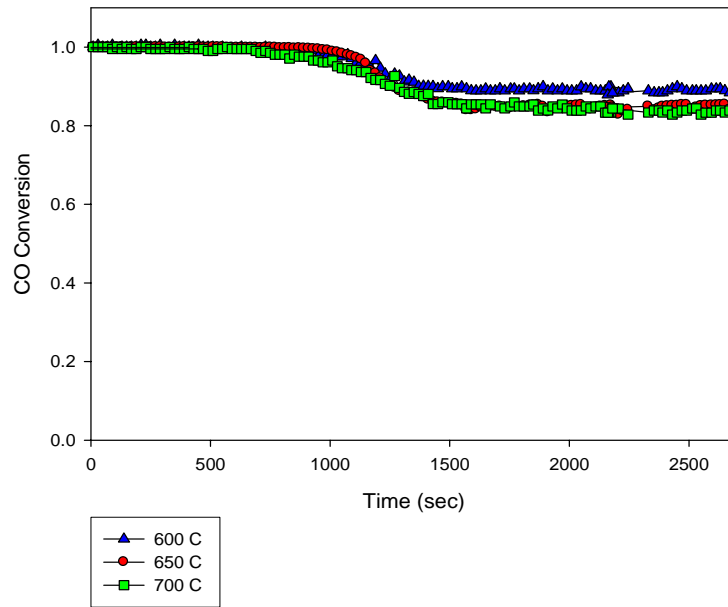


Figure 33: Effect of temperature on the CO conversion (S/C ratio= 3:1, Pressure = 300 psig)

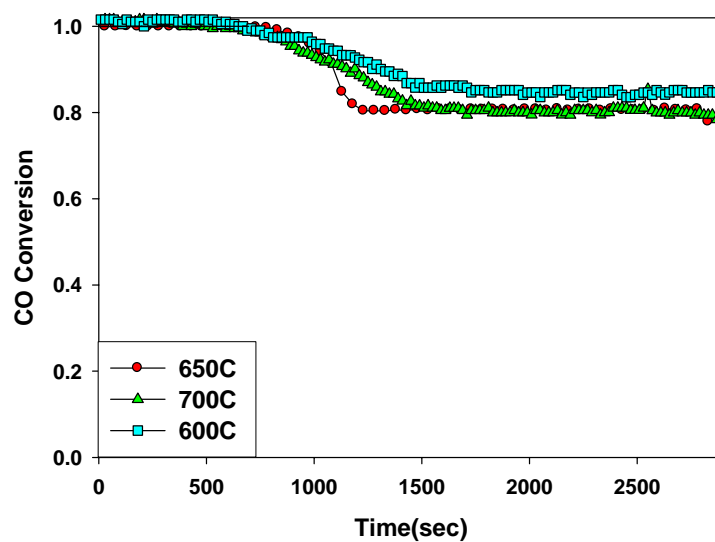


Figure 34: Effect of temperature on the CO conversion (S/C ratio= 2:1, Pressure = 300 psig)

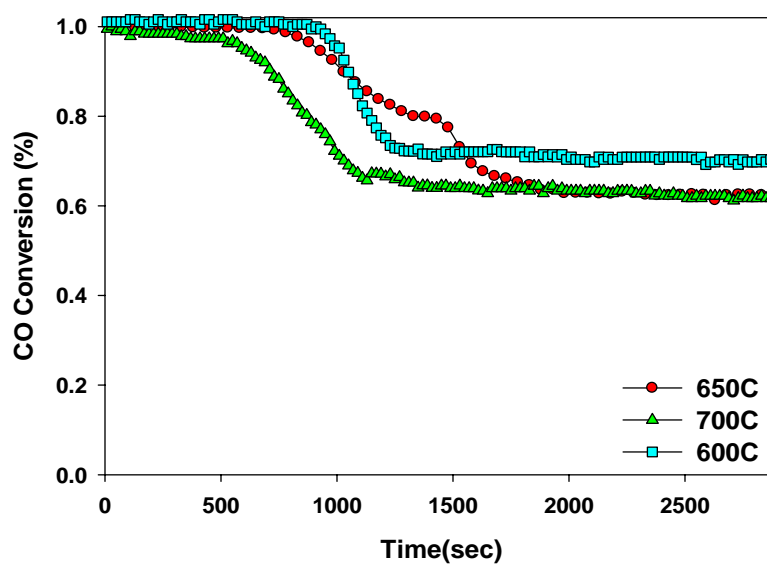


Figure 35: Effect of temperature on the CO conversion (S/C ratio= 1:1, Pressure = 300 psig)

CONCLUSIONS

It was observed that the CO₂ released during the in-situ calcination causes the deactivation of the iron oxide WGS catalyst by changing the active phase of the catalyst from magnetite (Fe₃O₄). Intermediate catalyst pretreatment helps prevent its deactivation by reducing the catalyst back to its active magnetite (Fe₃O₄) form. Multicyclic runs, which consist of combined WGS/carbonation reaction followed by in-situ calcination with a subsequent catalyst pretreatment procedure sustains the catalytic activity and prevents deactivation. The water gas shift reaction was studied at different temperatures, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0 - 300 psig. The CO conversion was found to increase with pressure, S/C ratio and temperature upto an optimum temperature. The partial pressure ratios of the products to the reactants were computed and found to lie within the equilibrium values. The extent of the combined water gas shift and carbonation reaction was found to increase with the increase in pressure and S/C ratio. At atmospheric pressure the CO conversion during the initial stage of the reaction decreases with the increase in temperature while the post breakthrough region increases with the increase in temperature. At higher pressures the CO conversion increases with the decrease in temperature for the entire breakthrough curve. Future work will involve studying the water gas shift reaction in the absence of a catalyst with the PCC sorbent in the system. This mode of operation will obviate the need for a catalyst thus reducing the cost and operating issues including catalyst deactivation.

Conference Presentation, Journal Papers and Patent Applications

This project has resulted in following conference proceeding, journal paper and patent application submission during the reporting period:

- Iyer, M.V; Ramkumar S.; Wong, D.; and Fan L.-S. “Enhanced Hydrogen Production with in-situ CO₂ capture in a Single Stage Reactor”. Presented at 23th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September **2006**, Paper 5-5..
- Sakadjian B. S. Iyer M.V., Gupta H., and Fan L.-S. “Kinetics and Structural Characterization of Calcium-based Sorbents under Sub-atmospheric Conditions for High-Temperature CO₂ capture Process” *Ind. Eng. Chem. Res.*, (*in press*) **2006**.
- Fan, Liang-Shih; Gupta, Himanshu; and Iyer, Mahesh V. “Separation of Carbon Dioxide (CO₂) from Gas Mixtures by Calcium Based Reaction Separation (Cars-CO₂) Process”. **United States Patent Application No. 11/255,099** filed on Oct 20 2005 (*Continuation in Parts*).

- Fan, Liang-Shih; Gupta, Himanshu; and Iyer, Mahesh V. “Regeneration of Calcium Sulfide to Mesoporous Calcium Carbonate using Ionic Dispersants and Selective Reclamation of Unreacted Calcium from Calcium-containing Solid Mixtures to Maximize Calcium Conversion and Prevent Recycling of Inerts” *United States Patent Application No. 60/694,702* filed in June 2005.

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